PATENT SPECIFICATION (11) 1 504 128

1 504 128

(21) Application No. 26736/74 (22) Filed 17 June 1974

(23) Complete Specification filed 11 June 1975

(44) Complete Specification published 15 March 1978

(51) INT CL² C08L 3/00, 1/26; D21H 3/80

(52) Index at acceptance
C3U 10X 12A3B 12A4 12B1A3 12B1AX 12B1B3A 12B2K 2AX
C3F 326 431 43Y 545 600
D1B 2D 2F 2G

(72) Inventor RAYMOND PETER AMOS

(19)

(54) SURFACE SIZING COMPOSITIONS

(7) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London SW1P 3JF, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to paper treatment and more particularly to an aqueous surface-sizing composition for paper, to the application of the composition and to the paper so obtained.

Paper is sized during manufacture in order to reduce its water absorbency and to increase the strength of the paper sheet. Sizing is conventionally carried out by addition of rosin and alum to the paper stock before formation of the paper sheet, i.e. at the wet end of the paper-making process. This method gives an acid sheet, and the acidity is deleterious to both the strength and the whiteness of the paper. An acid backwater is also obtained which gives rise to corrosion problems with the paper-making machinery.

It has now been found that a paper sheet having improved strength, ageing and brightness properties is obtained by surface sizing the preformed paper with a neutral or only mildly acid or alkaline, stabilised, aqueous sizing composition based on alum and soaps, rosins or similar compounds containing carboxylic acid groups.

According to the present invention there is provided a neutral or only mildly acid or alkaline (as hereinafter defined) aqueous surface-sizing composition for paper which comprises an aqueous solution containing

(i) a low viscosity (as hereinafter defined) grade of sodium carboxymethyl cellulose

or (ii) modified (as hereinafter defined) or unmodified starch;

(iii) alum;

and (iv) a carboxylic acid group-containing compound consisting of rosin, maleinised rosin, an alkali metal soap (as hereinafter defined) or maleinised petroleum resin;

in the proportions 0.8 to 2.0 of (i) or 1.0 to 4.0 of (ii)), 0.08 to 0.12 of (iii) and 0.8 to 0.12 of (iv) by weight, the total concentration of these components in the solution being from 10.0 to 1.0% by weight.

By "only midly acid or alkaline"' we mean having a pH in the range 4 to 10.

The preferred compound in (iv) above is maleinised rosin.

The ratio of the three components of the sizing composition is critical, and it is preferred that the proportion of components (i) or (ii), (iii) and (iv) respectively is 1.0:0.1:0.1 by weight.

The sodium carboxymethyl cellulose (SCMC) which is used must be a low viscosity grade, by which we mean that a 3% by weight aqueous solution has a viscosity at 20°C of 10 to 55 centipoises. If the viscosity is outside this range the composition has little or no sizing effect.

Increases in the proportion of component (iv) above that specified also adversely affect the sizing efficiency.

Although amounts of alum above the upper limit of 0.12 relative to the other two components can be tolerated in some cases, the increased acidity and lower colloidal stability of the resulting composition makes such usage undesirable.

A wide variety of different starches, both unmodified and modified, can be used. By modified starches we mean those starches in which the molecular weight of the material and/or the viscosity of its aqueous solutions relative to those of the unmodified material has been altered by treatment, for example, with sodium hypochlorite or enzymes. Insoluble starches have to be brought into solution in water by heating at temperatures up to the boiling point before the remaining components

of the sizing compositions can be incorporated.

By alkali-metal soap we mean the sodium or potassium salts of saturated or unsaturated aliphatic monocarboxylic acids containing from 8 to 22 carbon atoms and particularly the mixtures of such salts obtained by the saponification of natural fats and oils which are glycerides of such carboxylic acids. Examples of alkali metal soaps are sodium stearate, sodium palmitate and sodium oleate.

The sizing compositions according to the present invention are compatible with other hydrocolloids, for example, polyvinyl alcohol or alginates, which can be used with the compositions if desired. The compositions are also compatible with stilbene-based fluorescent brightening agents, which exhibit a greater effective brightness under the higher pH conditions existing in these compositions.

In preparing the sizing composition the order of mixing of the components is important, because the addition of alum solution directly to a solution of rosin, soap or the like gives a precipitate, and this must be avoided.

According to a further feature of the present invention there is provided a method for the preparation of the sizing compositions hereinbefore described which comprises adding an aqueous solution of components (i) or (ii) and (iv) as hereinbefore described to an aqueous alum solution, or by adding the alum solution to a solution of the other components.

The sizing compositions obtained according to the above-defined method are generally stable at pH values in the range 5 to 9. A pH of 6 to 8 is preferred, and the pH of the compoistions can be adjusted by addition of a base, for example, ammonia or sodium hydroxide. Should the composition show signs of instability as shown by formation of a precipitate, re-dissolution can usually be brought about by addition of a base, preferably ammonia, with stirring.

Application of the sizing composition takes place at the size press or calender stack, i.e. after formation of the paper sheet and partial drying thereof. Pick-up of the sizing composition is influenced by the nature of the base paper and the size press conditions, but in general an application of the composition equivalent to at least 0.3 g/m² of the solid components thereof is necessary for efficient sizing. The strength of the sizing composition solution can be varied between wide limits, provided that the proportions of the three components is kept within the ranges defined above.

Sizing can be carried out at normal room temperatures or at an elevated temperature, for example, up to 55°C or higher.

The invention can also be adapted to include the simultaneous sizing and dyeing of paper, by incorporating a water-soluble dyestuff into the sizing composition. Basic, acid and direct dyestuffs can all be used, provided that certain adjustments to the formulation of the sizing composition are made in order to maintain colloidal stability.

When basic dyestuffs are to be incorporated into the sizing composition, the latter cannot contain sodium carboxymethylcellulose because of chemical interaction between the basic groups of the dyestuff and the carboxylic acid groups in the cellulose derivative. It is therefore necessary to use starch or modified starch in the presence of basic dyes.

Sodium carboxymethylcellulose can be used with acid or direct dyes, although starch is preferred.

When formulating a combined sizing and dyeing composition with acid or direct dyes, an alkali, preferably, ammonia, is added to the sizing emulsion and a dilute (ca 3%) aqueous solution of the dyestuff is stirred in. Alternatively, the alkali can be added to the dyestuff solution before the latter is mixed into the sizing emulsion. The pH of the final composition must be at least 7. If desired, additional alum can be incorporated in the sizing emulsion before the dyestuff solution is added. Dye-fixing agents which are compatibile with the system may also be used, although higher fixation may be accompanied by a weaker shade.

In the case of basic dyes, the sizing composition is prepared using additional starch, conveniently double the normal amount, in order to achieve the necessary stability of the composition. A dilute (not exceeding 3%) aqueous solution of the basic dyestuff is then added to the sizing composition with stirring. The pH of the final composition is on the acid side, usually 4—5.

Satisfactory wet fastness results are generally obtained with direct and basic dyestuffs by the combined sizing/dyeing process according to the present invention. Usually a value of 3—4 or better on a 1—5 scale (5 represents maximum fastness) is achieved.

The combined sizing/dyeing process has the advantages that approximately half the amount of dyestuff can be used to achieve the same depth of shade obtained by conventional wet-end dyeing, and colour changes can be made more rapidly than with the latter method. It is also desirable to have the wet-end free from dyestuffs, as the difficulty of disposing of a large volume of coloured effluent is thereby avoided.

The present invention also includes the sized paper obtained by applying to paper a sizing composition as hereinbefore described.

The invention is illustrated by the following Examples in which parts and percentages are by weight.

Example 1.

An aqueous sizing composition containing starch (Viscosol (Registered Trade Mark) 220; a 10% aqueous solution has a viscosity of 11 centipoises at 20°C), rosin and alum in the proportions 1.0:0.1:0.1 was prepared

by cooking the starch in water to bring it into solution, then adding and mixing in 2½% aqueous rosin solution, followed by 5% aqueous solution of alum and dilution to the desired strength. Solutions of different strength were applied to paper (bleached sulphite pulp, weight 55 gm/²) for different pick-up values, the paper was dried and the sizing efficiency was estimated by measurement of the 1 minute Cobb Value. Results are as follows:

Sizing composition applied as:	Pick-up (g/m^2)	1 min. Cobb Value
1.2% solution	0.3	16.7
0.9% ,,	0.225	23.0
0.6% ,,	0.15	59.0

The lower the Cobb Value, the more efficient is the sizing (Cobb Value is a measure of water pick-up by the sized paper). In general, Cobb Values of up to 30 are acceptable. The final value of 59.0 in the above table is unacceptable and shows the result of applying insufficient sizing composition.

Example 2.

An aqueous composition similar to that described in Example 1 but using Viscosol 220 starch, rosin and alum in the proportions 4.0:0.1:0.1 was made up. The total concentration of solids in the solution was 4.2% and its pH was 5.5. On application to bleached sulphite pulp (BSP) paper (55g/m²) at a pick-up of 1.1gm/², the dried paper has a 1 minute Cobb Value of 24.0.

Example 3.

Aqueous sizing compositions containing SCMC (Cellofas (Registered Trade Mark) B5; a 3% aqueous solution has a viscosity of 10—55 centipoises at 20°C) soap flakes (essentially sodium palmitate/stearate) and alum were made up and applied to BSP paper (55g/m²). Results are as follows:

	Proportions of components			Sizing Composition supplied as:	Pick-up (g/m^2)	pH of Comp.	1 min. Cobb Value
	Cellofas B5	Soap Flakes	Alum				
Comparative test	1.0	0.2	0.1	1.3% solution	0.3	6.3	Unacceptable
	1.0	0.1	0.1	1.2% solution	0.3	5.5	20.0

The above results illustrate that the use of too high a proportion of soap relative to SCMC and alum gives paper having an unacceptably high Cobb Value.

Example 4.

Aqueous compositions using Cato (Registered Trade Mark) 110 starch (a 10% aqueous solution has a viscosity of 74 centipoises at 20°C), rosin and alum were made up and applied to BSP paper (55gm/²).

Results are as follows:

Proportions of components			Sizing Composition applied as:	Pick-up (g/m^2)	pH of comp.	1 min. Cobb Value
Cato 110	Rosin	Alum				
4.0	0.1	0.1	4.2% solution	1.1	5.5	20
1.0	0.1	0.1	1.2% solution	0.3	5.5	18

Example 5.

An aqueous solution using Enziplast A 556 starch (a 5% aqueous solution has a viscosity of 2300 centipoises and a 1% aqueous solution has a viscosity of 30 centipoises, at 20°C) rosin and alum in the proportions 1.0:0.1:0.1 was made up at a strength of 1.2% and applied to BSP paper (55g/m²). The pH of the

composition was 5.7, and the pick-up was 0.3g/m². The sized paper had a 1 minute Cobb Value of 20.

Example 6.

An aqueous composition using Pregelatinised Farina starch (a 1% aqueous solution has a viscosity of 30 centipoises at 20°C), rosin and alum in the proportions 1.0:0.1:0.1 was made up at a strength of 1.2% and applied to BSP paper (55g/m²). The pH of the composition was 4.6, and the pick-up was 0.3g/m². The sized paper had a 1 minute Cobb Value of 18.0.

Example 7.

An aqueous sizing composition similar to that described in Example 1 using Viscosol 220 starch, rosin and alum in the proportions 1.0:0.1:0.1 was made up and applied to BSP paper (55g/m²) at different concentrations.

Results are as follows:

Sizing composition applied as:	Pick-up (g/m²)	1 min. Cobb Value
4.8% solution	1.1	15.0
2.4% ,,	0.6	16.2
1.2% ,,	0.3	17.8

Example 8.

Aqueous sizing compositions were made up using sodium carboxymethylcellulose (Cellofas B6; see Example 3), rosin and alum in the proportions indicated below and applied to BSP papers (55g/m²) as a 1.2% solution.

Results are as follows:

	Proportions of components			Pick-up (g/m²)	1 min. Cobb Value
	Cellofas B5	Rosin	Alum		
Comparative test	1.0	0.13	0.1	0.3	25
	1.0	0.12	0.1	0.3	25
	1.0	0.11	0.1	0.3	32
	1.0	0.09	0.1	0.3	22
	1.0	0.08	0.1	0.3	30
Comparative test	1.0	0.07	0.1	0.3	49.6

These results illustrate the sudden and unacceptable fall off in sizing efficiency when the proportion of rosin is reduced below the minimum amount according to the present invention. Excessive resin concentration produces a colloidal instability in the sizing emulsion with a consequent risk of precipitation occurring on storage.

Example 9.

This example illustrates combined sizing and dyeing of paper using direct dyestuffs.

Two different systems were used, as follows:

System 1:—0.25% of dyestuff and 0.25% of alum were added to a sizing emulsion of 2% Viscosol 220 starch, 0.2% alum and 0.2% rosin to which had previously been added a large excess (2.5%) of concentrated aqueous ammonia solution to ensure a stable composition with a wide range of dyes.

System 2:—0.25% of dyestuff and 0.25% of a dye fixing agent (50% aqueous solution of a methylol dicyandiamide resin) were added to the sizing emulsion used in System 1 to which had previously been added a large excess (2.0%) of concentrated aqueous ammonia solution.

The rosin used in this and subsequent examples is Pexlim (Registered Trade Mark) size, a fortified rosin.

The following results were obtained:

Dyestuff (0.25% on weight of sizing emulsion unless otherwise indicated).	System 1		System 2	
	Wet Fastness	1 Minute Cobb Value	Wet Fastness	1 Minute Cobb Value
Chlorazol Yellow GP (C.I. Direct Yellow 11)	5	14	5	17
Durazol Red 2B (C.I. Direct Red 81)	3	15	4–5	16
Durazol Blue 10GP	5	15	5	14
Durazol Yellow KTP	4	13	4	21
Durazol Yellow FR	3–4	14	4–5	16
Durazol Orange 2G (C.I. Direct Orange 34)	4	13	4–5	16
Chlorazol Scarlet 48 (0.375%)	4–5	19	5	18
Durazol Green 2GP	4–5	20	5	20
Chlorazol Black 2G Liquid (1.8%)	4–5	18	5	19

(The words "Chlorazol" and "Durazol" are Registered Trade Marks).

Example 10.

This Example illustrates the effect of increasing concentrations of dyestuff on the wet fastness of dyed and sized paper.

The dyestuff Chlorazol Blue G (C.I. Direct Blue 10) was added to a sizing emulsion of 2% Viscosol 220 starch, 0.2% alum and 0.2% rosin containing 2% concentrated aqueous ammonia solution, to give the concentrations in the emulsion indicated below.

Results were as follows:

Dyestuff concentration (%)	Wet Fastness	1 minute Cobb Value
0.05	5	21
0.1	5	18
0.25	4–5	18
0.5	3	17
1.0	2–3	19

Example 11.

This Example illustrates the effect of variations in the composition of the sizing emulsion on the fastness properties of dyed and sized paper.

In each case the emulsion contained 1.5% Durazol Red 2B Liquid (containing 33% by weight of dyestuff) and was made up by adding the specified quantity of ammonia to the sizing emulsion before finally adding the dyestuff.

Results were as follows:—

% Starch	% Alum.	% Rosin	% Concentrated ammonia soln.	1 minute Cobb Value	Wet Fastness	°SR
4	0.4	0.4	0.5	27	3.4	35
4	0.4	0.4	0.75	16	3–4	30
2	0.4	0.4	0.75	15	4–5	30
2	0.3	0.3	0.5	17	4	30

°SR=Schopper Riegler Degree of Freeness of the bleached sulphite pulp used to form the paper.

Example 12.

This Example illustrates the effect of different furnishes and degree of beating on the sizing efficiency of dyed and sized paper.

In each case the emulsion contained 1.5% Durazol Red 2B Liquid added to a sizing emulsion of 2% Viscosol 220 starch, 0.2% alum and 0.2% rosin, previously made alkaline by the addition of 0.75% of concentrated aqueous ammonia solution. 110 g/m² hand sheets were produced and sized/dyed with the emulsion. Results were as follows:—

Furnish	°SR	1 min. Cobb Value
1. Unbleached sulphite	26	18
2. Semi-bleached Kraft	27	21
3. Bleached Kraft	30	21
4. Bleached Sulphite (BSP)	40	22
5. BSP+10% Broke from (4)	40	29

Example 13.

This Example illustrates the effect of increasing ammonia concentration on the stability of the dyeing/sizing emulsion.

In each case the emulsion contained 1.5% Durazol Red 2B Liquid additional to the sizing emulsion of 2% Viscosol 220 starch, 0.2% alum and 0.2% rosin, the ammonia being added to the sizing emulsion before adding the dyestuff.

Results were as follows:—

% Concentrated ammonia	pH	Comment
0.0	4.4	Gelatinous precipitate
0.05	5.1	Still unsuitable for size press.
0.1	7.5	Stable solution suitable for size press.
0.2	9.2	,,
0.5	9.7	,,

Example 14.

This Example illustrates combined sizing and dyeing of paper using basic dyestuffs. Each formulation was made up by adding a dilute aqueous solution of the basic dyestuff to the sizing composition.

Results were as follows:—

Dyestuff	% Dye	% Starch	% Rosin	% Alum.	% Dye Fixing agent*	1 min. Cobb Value	Wet Fastness
Victoria Blue B (C.I. Basic Blue 26)	0.25	2.5	0.125	0.125	0.125	19	5
Auramine O (C.I. Basic Yellow 2)	0.125	2.5	0.125	0.5	0.5	17	4
Chrysoidine Y Liquid (C.I. Basic Orange 2) (containing 47% by weight of dyestuff)	0.25	2.5	0.125	0.5	0.5	15	3—4
Methylene Blue B Liquid (C.I. Basic Blue 9) (containing 50% by weight of dyestuff)	0.25	2.5	0.125	0.125	—	16	4

* The dye-fixing agent used was based on a naphthalene sulphonic acid/formaldehyde condensate.

WHAT WE CLAIM IS:—

1. A neutral or only mildly acid or alkaline (as hereinbefore defined) aqueous surface-sizing composition for paper which comprises an aqueous solution containing

(i) a low viscosity (as hereinbefore defined) grade of sodium carboxymethyl cellulose

or (ii) modified (as hereinbefore defined) or unmodified starch;

(iii) alum;

and (iv) a carboxylic acid group-containing compound consisting of rosin, maleinised rosin, an alkali metal soap (as hereinbefore defined) or maleinised petroleum resin;

in the proportions 0.8 to 2.0 of (i) or 1.0 to 4.0 of (ii), 0.08 to 0.12 of (iii) and 0.8 to 0.12 of (iv) by weight, the total concentration of these components in the solution being from 10.0 to 1.0% by weight.

2. A composition as claimed in claim 1 wherein component (iv) is maleinised rosin.

3. A composition as claimed in claim 1 or claim 2 wherein the proportion of components (i) or (ii), (iii) and (iv) respectively is 1.0:0.1:0.1 by weight.

4. A composition as claimed in any one of claims 1 to 3 having a pH of 6 to 8.

5. An essentially neutral aqueous surface-sizing composition for paper substantially as hereinbefore described with reference to the foregoing Examples 1 to 8.

6. A method for the preparation of the sizing composition claimed in claim 1 which comprises adding an aqueous solution of components (i) or (ii) and (iv) as defined in claim 1, to an aqueous alum solution, or *vice versa*.

7. A method as claimed in claim 6 and substantially as hereinbefore described with reference to the foregoing Example 1.

8. An essentially neutral surface-sizing composition for paper whenever obtained by a method as claimed in claim 6 or claim 7.

9. A composition as claimed in any one of claims 1 to 4 which also contains an acid or direct dyestuff, the pH of the concentration being at least 7.

10. A composition as claimed in claim 9 wherein components (ii), (iii) and (iv) as defined in claim 1 are employed.

11. A composition as claimed in claim 1 or claim 2 wherein components (ii), (iii), and (iv) as defined in claim 1 are employed and which also contains a basic dyestuff, the compositions having an acid pH.

12. A composition as claimed in claim 11 wherein the pH is 4—5.

13. A composition as claimed in claim 9 and substantially as hereinbefore described with reference to the foregoing Examples 9 to 13.

14. A composition as claimed in claim 11 and substantially as hereinbefore described with reference to the foregoing Example 14.

15. A method for the preparation of a composition as claimed in claim 9 which comprises first adding an alkali to a composition as claimed in any one of claims 1 to 4, followed by addition of a dilute aqueous solution of an acid or direct dyestuff, the amount of alkali being such that the pH of the final composition is at least 7.

16. A method for the preparation of a composition as claimed in claim 9 which comprises adding an alkali to a dilute aqueous solution of an acid or direct dyestuff, the resulting solution then being added to a composition as claimed in any one of claims 1 to 4, the amount of alkali being such that the pH of the final composition is at least 7.

17. A method for the preparation of a composition as claimed in claim 11 which comprises adding a dilute aqueous solution of a

basic dyestuff to a composition as claimed in claim 1 or claim 2, the final composition having an acid pH.

18. A method as claimed in claim 15 and substantially as hereinbefore described with reference to the foregoing Examples 9 to 13.

19. A method as claimed in claim 17 and substantially as hereinbefore described with reference to the foregoing Example 14.

20. A surface-sizing/dyeing composition for paper whenever obtained by a method as claimed in any one of claims 15 to 19.

21. Paper whenever sized with a composition as claimed in any one of claims 1 to 5 and 8.

22. Paper whenever sized and dyed with a composition as claimed in any one of claims 9 to 14 and 20.

D. VINCENT,
Agent for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1978.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

? ..li

1/1 - (C) WPI / DERWENT

AN - 98-603601 [51]

AP - JP970081489 970331

PR - JP970081489 970331

TI - Hydrolytic sheet - includes base material sheet of water-dispersive fibre, and carboxyl methyl cellulose and/or its salt; and a liquid component

IW - HYDROLYSIS SHEET BASE MATERIAL SHEET WATER DISPERSE FIBRE CARBOXYL METHYL CELLULOSE SALT LIQUID COMPONENT

PA - (UNIC-N) UNI-CHARM KK

PN - JP10273892 A 981013 DW9851 D21H17/27 008pp

IC - D04H1/04 ; D06M11/76 ; D21H17/27 ; D21H17/63

AB - J10273892 A base material sheet consists of a water-dispersive fibre, and carboxyl methyl cellulose and/or its salt. A liq. component consists of water, and one or two or more water-soluble alkaline metal salts and/or water-soluble ammonium salts having 0.5 wt.%-aq. soln. pH of 5 or more to 9 or less. The liq. component is impregnated into the base material sheet. to form a wet state.

- Also claimed is that the prodn. comprises: (a) impregnating the liq. component in the base material sheet; (b) forming the wet state.
- USE - The method produces the hydrolytic sheet used for treating a toilet, a purifier, or sewage.
- ADVANTAGE - The alkaline metal salt and/or the ammonium salt depresses the electrolytic dissociation of the carboxy methyl cellulose and/or its salt. The resulting hydrolytic sheet has good wet tenacity. The sheet in flowing water rapidly decreases the concn. of the alkaline metal and/or the ammonium salt to promptly swell or dissolves the carboxymethyl cellulose and/or its salt, collapsing the structure of the sheet to disperse the fibre.
- (Dwg.0/0)